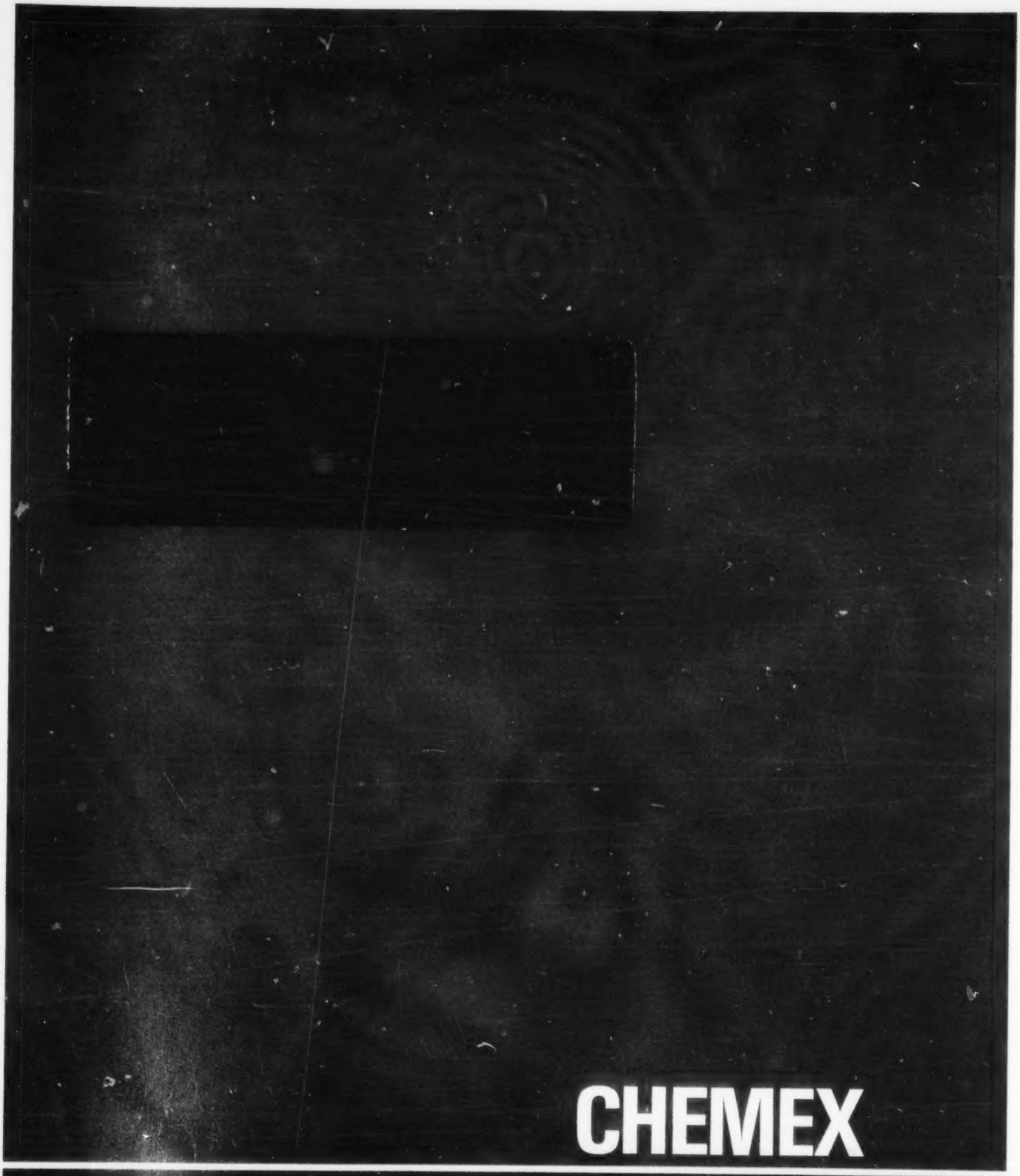
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A STUDY OF ASPHALTENE FLOCCULATION IN HEAVY OIL AND ASPHALT SOLUTIONS

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FINAL REPORT

B.J. Fuhr
L. Coates
L. Klein
C. Reichert

Alberta Research Council
Oil Sands and Hydrocarbon Recovery
P.O. Box 8330, Postal Station F
Edmonton, Alberta
T6H 5X2

J. Steppler

Chemex Labs (Alberta) Ltd.
2021 - 41 Avenue N.E.
Calgary, Alberta
T2E 6P2

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EXECUTIVE SUMMARY

Two different experimental set-ups are described for determining the onset of asphaltene precipitation in heavy oil solutions. The first system, applicable to experiments under ambient conditions, employs a visible spectrophotometer with flow-through cell. The second, which must be used for experiments at pressures above atmospheric, employs a fiber optics probe which can operate in the visible and near infrared region.

A number of heavy oil and asphalt systems were studied using these experimental techniques. First of all, the degree of chemical alteration of fireflood oils compared to primary production oils was found to correlate with the asphaltene flocculation results. Secondly, it was found that both CO_2 and propane dissolved in heavy oil solutions increase the tendency for asphaltene precipitation. This effect is reduced with an increase in temperature, presumably because of a reduction in the solubility of these gases. Thirdly, natural gas liquids of relatively high aromatics content have a low tendency to precipitate asphaltenes, and would therefore make good heavy oil diluents. Finally, there appears to be a correlation between asphalt stability, as measured by a standard settling test, and the asphaltene precipitation tendency as determined by the flocculation test.

Sommaire Executif

Cet article présente deux travaux expérimentaux qui visent à déterminer l'apparition des précipitations d'asphaltène dans les solutions aqueuses d'huile lourde. Dans l'une des expériiences, effectuée dans une cellule transparente et à la temperature ambiante, on a utilisé un spectrophotomètre. Pour la deuxième série d'expériences, qui se sont déroulées dans des conditions de température et de pressions élevées, le signal lumineaux a été transmis au spectrophotomètre à l'aide de fibres optiques, qui transmettent le spectre lumeneaux et infra-rouge.

On a étudié plusiers combinaisons d'huile lourde et d'asphaltène à l'aide des méthodes mentionnées ci-dessus. Premiére conclusion: le degré d'altération chimique du pétrole, obtenu par combustion sousterraine, est similaire à celui du pétrole obtenu durant la production naturelle. Deuxième conclusion: tant le bioxide de carbone que le propane dissous dans les solutions d'huile lourde ont augmenté les tendances de précipitation de l'asphaltène. Pourtant, cet effet diminue au fur et à mesure que la température s'élève, supposément à cause d'une dimution de la solubilité de ces gaz.

Troisième conclusion: les composants liquides du gas naturel à haute teneur en fractions aromatiques ont motré une faible tendance à précipiter l'asphaltène. Par conséquent, ces composants peuvent être utilisés comment solvents d'huile lourde.

Finalement, une corrélation semble exister entre la stabilité de l'asphaltène, mesurée par un test standard de sédimentation et la tendance des asphaltènes de précipiter, mesurée à l'aide d'un test de floculation.

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INTRODUCTION

The determination of the onset of asphaltene flocculation in heavy oil solutions can provide valuable and useful information about the oils, such as the thermal alteration of oils due to recovery operations, refinery upgrading methods, their compatibility with diluents and effects of various additives during insitu recovery.

Reichert et al. (1) developed a relatively simple, inexpensive asphaltene flocculation test for measuring the compatibility of diluent-bitumen mixtures. This method is based on work previously reported by Bichard (2) and Hotier and Robin (3). Waxman et al. (4), using a similar method studied the alteration of heavy oils during a steam-based production process. Lambert and Holder (5) studied how thermal conversions of residues during upgrading operations affect their stability.

The injection of gaseous additives such as carbon dioxide and propane along with hot water or steam into a heavy oil formation has the potential of recovering more oil than the use of hot water or steam alone. One of the potential problems with the use of gases is the possibility of asphaltene precipitation. The investigation of the effect of gases requires experiments to be conducted under pressure. Lhioreau et al. (6) developed a system for measuring the amount of asphaltenes precipitated from a light crude using propane, pentane, hexane and heptane at pressures up to 34 MPa. Burger and Robin (7) and Fuhr et al. (8) extended the standard asphaltene flocculation test to elevated temperatures and pressures using a fiber optics monitor in a pressure vessel. Hirschberg et al. (9) visually determined the onset of asphaltene flocculation upon contact of light crudes by gases. Rahimian (10) determined pressure and temperature ranges in which asphaltenes were precipitated from live oils by measuring the decrease in transmittance of light through two inspection windows in a pressure vessel.

Solvent dilution is often used to reduce the viscosity of heavy oil and bitumen in order to facilitate their production and transportation. The solvent may be added to the production well to increase the efficiency of the pump, to treaters to aid in the separation of solids and water or to the final product to reduce

the viscosity for transportation by truck or pipeline. Some diluents, however, may lead to the precipitation of asphaltenes from the bitumen which will cause serious problems for the plant or pipeline operator. Often the best diluents are in short supply, which will force a plant operator to use a poor one, or to work with a blend of two or more diluents. It is therefore desirable to have available simple test methods for evaluating the solvating power of diluents for heavy oil and for predicting the viscosity of mixtures of diluents and heavy oil. Ridley et al. (11) compared the solvent strengths of condensates and their blends for use as diluents in the transportation of heavy oil. It would be useful to evaluate lighter materials than these, such as natural gas liquids (NGL's) which would require runs to be made at pressure somewhat above atmosphere.

A test method was developed by Plancher (12) to evaluate the relative degree of dispersion of asphaltenes in paving asphalts. This dispersion is considered to be a function of the compatibility of the asphalt components which in turn is considered to be an important property that contributes to asphalt durability. A technique similar to that reported by Bichard (2) was used by Heithaus (13) to characterize dispersions in asphalts, and related to other properties of the asphalts. Since the onset of asphaltene precipitation generally provides an indication of the solvating power of the oil for its own asphaltenes, this value should also indicate the compatibility of the components in the oil.

In summary, the objectives of the present work were the following:

1. To compare the flocculation data of a number of heavy oils and residues from different sources, and to correlate these results with known background of the samples.

2. To determine the relative effects of dissolved CO_2 and propane on the flocculation of asphaltenes in a heavy oil.

3. To determine the relative solvating power of some NGL's with respect to a heavy oil.

4. To investigate approaches for obtaining asphalt stability data from the asphaltene titration experiments.

EXPERIMENTAL

Equipment

A. Atmospheric experiments: The apparatus described previously (1,11) and illustrated in Figure 1, consisted of a Hewlett Packard 8450A UV-visible spectrophotometer fitted with a 1 mm optical path flow cell. The solution was circulated between a 150 mL Metrohm titration cell and the flow cell at a rate of 20 mL/min. through 3 mm ID Viton tubing by means of a peristaltic pump. The titrating solvent was added to the sample in the titration cell by means of an autotitrator in 1 mL increments every 30 s.

B. Pressure experiments: This apparatus, shown in Figure 2 and described previously (8), consisted of an Optical Waveguide Spectrum Analyzer equipped with a high pressure and temperature fiber optics probe with a 1-10 mm adjustable path length. A 350 mL Parr pressure vessel, fitted with a thermocouple, was used as a titration cell into which the titrant and gases were added. The titrant was pumped into the vessel at a rate of 2 mL/min. using a Milton Roy mini-pump, type NS1-33R. For temperatures below 70°C the pressure vessel was placed in a thermostated temperature bath; above this temperature a heating mantle was used. The data from the analyzer were collected with an AT&T PC6300 computer.

Procedures

A. Atmospheric experiments: Twenty-five mL of sample as a solution in the diluent of interest were placed in the titration cell and stirred. For Part 1 of the study, n-pentane was added and the absorbance monitored at 800 nm by the UV/vis spectrophotometer. The absorbance decreases due to sample dilution until the onset of particle formation, at which point (the end point) it increases due to the scattering of light by the asphaltene particles. If these end points are plotted as shown in Figure 3, the slope provides a scale of the relative solvating power of the diluent with the higher slope representing the better solvent. A negative slope indicates a solvent which will precipitate asphaltenes at some concentration without addition of pentane. The intercept, or flocculation threshold indicates the

amount of titrant required to initiate the precipitation of asphaltenes in the oil in the absence of any solubilizer. In other words, it is indicative of the solubilizing power of the oil for its own asphaltenes. For Part 4 of the study, the fiber optics probe was placed directly in the titration vessel to make the measurements in situ.

B. Pressure experiments: For Part 2 of the study, twenty-five mL of a solution of the heavy oil sample in toluene were placed in the pressure vessel which in turn was either placed in the temperature bath or surrounded by a heating mantle. The solution was stirred and the whole assembly allowed to equilibrate at the set temperature. The solution was then pressurized with CO_2 or propane from a gas cylinder to a selected pressure for a period of 4 min. The valve was closed and the solution titrated with n-heptane. The absorbance was monitored at 900 nm using the fiber optics probe and the data collected on the computer. End points were determined from these data and plots similar to those for the atmospheric experiments were constructed.

For Part 3 of the study, known amounts of NGL were added to the heavy oil in the pressure vessel, and the system pressurized with He.

Materials

A Lloydminster heavy oil obtained from the Alberta Research Council Oil Sands Sample Bank was used in all experiments. The toluene, n-pentane and n-heptane were ACS certified reagent grade solvents. The primary production and fireflood oils were obtained from another study by Reichert et al. (14). The vacuum bottoms feedstocks were obtained from CANMET. A cylinder equipped with eductor tube was used to supply the CO_2 or propane required for the experiments. The NGL's and their analyses were received from Chemex Labs. The asphalt samples were obtained from H. Plancher at the Western Research Institute, Laramie, WY.

1. COMPARISON OF ASPHALTENE DATA FOR DIFFERENT HEAVY OILS AND RESIDUES

Results and Discussion

The data obtained for a primary production heavy oil and three fireflood produced oils from the same field are shown in Table 1A. Standard deviations are also given for the data to demonstrate their significance. The corresponding plots are given in Figure 3. It can be seen from these data that the F-1 fireflood samples have significantly lower intercepts than that of the P-1 primary production sample. The F-2 fireflood sample, on the other hand is very nearly the same as the primary production. This indicates poorer solvating properties of the F-1 fireflood oils, and that changes have taken place. Similar types of changes were observed by Waxman et al. (4) in thermally produced Peace River bitumens. The slopes observed in the current work are not that different, indicating not surprisingly, that toluene has a similar solvating power for all the oils. The density, viscosity and distillation data for these four oils reported by Reichert et al. (14), and also shown in Table 1B correlate fairly well with the asphaltene titration data. The higher amount of naphtha in the F-1 samples results in a lower density and viscosity and in turn decreases the solvating properties of the oil for its own asphaltenes. The F-2 sample, however, is much the same as the primary production, and also has about the same solvating properties.

Similar asphaltene titration data for a series of vacuum bottoms feedstocks are shown in Table 2. These feedstocks were obtained from CANMET. Large differences are seen, particularly in the intercepts, indicating large differences in solvating powers, which could be related to upgrading conditions. Unfortunately, no other characterization data for these samples can be located. The results are presented here so that, should additional data be located, some useful correlations may be made.

Conclusions

The flocculation threshold as obtained from the asphaltene titration data described here appears to be related to the observed differences between the

primary production and fireflood produced heavy oils. The lower the density and viscosity, and higher the naphtha content the smaller is the flocculation threshold. In other words, the more likely are asphaltenes to precipitate from the oil.

2. EFFECTS OF CARBON DIOXIDE AND PROPANE ON ASPHALTENE PRECIPITATION

A. Carbon Dioxide

Results and Discussion

Before investigating the effect of CO_2 at elevated pressure on the initiation of asphaltene precipitation, the effect of pressure alone was determined and compared to previously published work. In all pressure vessel runs n-heptane was used as the titrant and toluene as the solvent. The results of the baseline atmospheric run at 15°C are shown by the line of highest slope in Figure 4. The slopes obtained for experiments conducted at pressures above atmospheric using the inert gas He, are shown in Table 3. There is no apparent change in the slope up to a pressure of 4.8 MPa (700 psi).

Burger and Robin (7) made similar asphaltene flocculation plots as a function of both temperature and pressure using an Athabasca bitumen. Unfortunately it is not possible to abstract just the pressure dependence from their data. Lhioreau et al. (6) found that the total amount of asphaltenes precipitated from a light crude using pentane decreased by about 30% in going from atmospheric to 35 MPa. These workers concluded that the asphaltene solubility increases with an increase in pressure. This effect was presumably not observed in the present work since the highest pressure investigated was only 4.8 MPa and any increase was probably hidden by experimental error.

The effect of CO_2 on toluene solutions of heavy oil which are titrated with heptane at 15°C is shown in Figure 4. The slopes are also indicated in Table 3. It can be seen that an increase in the CO_2 pressure results in a decrease in the slope, or a greater tendency for asphaltenes to precipitate. There will be a distribution of the CO_2 between the solution and the headspace in the pressure vessel, and it is expected that the amount of dissolved CO_2 will generally increase with increasing pressure. Data is available (15) which shows the increase in CO_2 dissolved in bitumen as the

pressure is increased. Similar behavior is expected for bitumen in toluene solutions.

Experiments were also carried out to determine whether CO_2 in the absence of heptane would precipitate asphaltenes from heavy oil solutions. This was accomplished at 15°C by increasing the CO_2 pressure at a rate of 0.28 MPa/min. (40 psi/min.) to a maximum of 5.6 MPa (820 psi). An example is shown in Figure 5. Absorbance begins at zero because the probe was initially not covered with solution. The increase in absorbance which follows up to 150 s is the time taken for the probe to become completely covered with solution, after which a small decrease is observed due to dilution of solution by CO_2. The sharp increase in absorbance at 1020 s, which corresponds to 4.7 MPa (680 psi) indicates the sudden appearance of a large amount of precipitate with consequent light scattering. These experiments were performed at the toluene in heavy oil concentrations shown in Table 4, and the points are indicated on the x-axis of Figure 4 indicating that flocculation is achieved without pentane. It can be seen that, when plotted this way, the higher the CO_2 pressure, the less dilution of the oil with toluene that can be carried out before the onset of asphaltene flocculation in the absence of n-heptane. There is a correspondence between these results and those of Ridley (11) who indicated that the poorer the solvent, the less dilution in a heavy oil that can be carried out before asphaltenes precipitate in the absence of n-pentane. In summary, the higher the CO_2 pressure, the poorer the solvating properties of the solution and the less it may be diluted before asphaltenes begin to precipitate. The pressures employed are all below the bubble point of CO_2 which is 5.2 MPa at 15°C.

Hirschberg et al. (9) did not observe any asphaltene precipitation in a light crude at 23°C even at a CO_2 pressure as high as 5.3 MPa (770 psi). The present results presumably differ because of the differences in the oils. Hirschberg did, however, observe flocculation when the crude was diluted in n-decane, which would render the solution a poor solvent for asphaltenes.

The effect of temperature on the asphaltene flocculation plots was studied at a CO_2 pressure of 2.8 MPa. The slopes are compared at three

temperatures in Table 3. Burger and Robin (7) found from similar plots with Athabasca bitumen that at a pressure of 7 MPa (but in the absence of CO_2) an increase in the temperature resulted in a decrease in the slope. This can be explained on the basis of a decrease in asphaltene solubility as the temperature increases, as reported by Mitchell and Speight (16), resulting in a greater tendency for precipitation. The fact that the present data show an increase in slope with increase in temperature indicates that the decrease in solvating power brought about by the CO_2 is more significant than that of the temperature effect on asphaltene solubility. Therefore, as the temperature is increased the solubility of CO_2 in solution decreases resulting in a decreased tendency for asphaltene precipitation. Other data (15) indicate a decrease in solubility of CO_2 in bitumen at a given pressure with an increase in temperature. It would be expected that bitumen in toluene solutions behave in a similar fashion.

B. Propane

The effect of propane on toluene solutions of heavy oil which are titrated with n-heptane at 15°C is shown in Table 5. Assuming that the amount of propane in solution is proportional to the pressure of the system, the slopes indicate that at 15°C the propane results in a decrease in solvating properties as the pressure is increased from 0.35 MPa to 0.52 MPa. The experiments performed at higher pressures resulted in considerable scatter and could not be used. Schwarz and Prausnitz (17) reported that ethane solubility in heavy oil increases with increase in pressure. Presumably propane exhibits similar behavior. It was also found that ethane is more soluble than CO_2, which may explain the lower slopes for propane at lower pressures compared to CO_2. In the absence of heptane, a 2.38 mL toluene per g oil solution oil begins to precipitate asphaltenes when the propane pressure reaches 0.79 MPa shown in Figure 6. This pressure happens to be the bubble point for propane. A similar finding was noted by Hirschberg et al. (9) for a neat light crude. At this pressure, the gaseous propane in the headspace of the pressure vessel immediately changes to a liquid which is miscible in the oil. This large increase in propane concentration in the oil is probably what results in an immediate precipitation of asphaltenes. Mitchell and Speight (16) showed that liquid propane results in

precipitation of a large amount of asphaltenes. Presumably with CO_2, a much higher pressure could be attained because of the higher bubble point of CO_2.

Turning to Table 5 again, upon increasing the temperature from 15 to 50°C, the trend is to an increased slope indicating better solvating properties. Again at higher pressures and temperatures, the data showed much scatter and could not be used. As in the case of CO_2, this increase in temperature probably results in a decrease in the solubility of propane in solution with a corresponding decrease in the tendency for asphaltene precipitation. Similar results were reported by Hirschberg et al. (9), who observed an increase in the propane pressure required to bring about the onset of precipitation in a neat light crude as the temperature was increased from 20 to 60°C. Schwarz and Prausnitz (17) did report that ethane solubility in heavy oil does decrease with increase in temperature. The same is probably true for propane.

Conclusions

Upon titration of heavy oil in toluene solutions with heptane, an increase in the CO_2 pressure of the system results in a greater tendency for asphaltene precipitation. At a given pressure this effect is reduced as the temperature is increased presumably because of the reduced solubility of CO_2 in the oil. At pressures greater than 3.5 MPa, but still below the bubble point of CO_2, asphaltenes will precipitate without the addition of heptane.

In the same heavy oil solutions, an increase in the propane pressure also results in an increased tendency for precipitation. At the bubble point of 0.79 MPa at 15°C propane immediately precipitates asphaltenes. At a given pressure, there is a slight decrease in precipitation tendency as the temperature is increased presumably due to the decreased propane solubility.

Recommendations

In order to better explain the CO_2 and propane results, data on the actual amount of the gases in solution should be determined.

3. EFFECT OF NATURAL GAS LIQUIDS ON ASPHALTENE PRECIPITATION

Results and Discussion

Two natural gas liquids (NGL's), whose component characterization as determined by gas chromatography are shown in Tables 6 and 7, were employed as diluents for the heavy oil. NGL-1 has an aromatics content of 0.45 mass fraction, whereas that for NGL-2 is only 0.04. The distribution of the small amount of paraffins in the former is a maximum at C_{11}, whereas that of the large amount of paraffins in the latter is a maximum at C_8. NGL-1 therefore, would be expected to be a better diluent for the heavy oil than NGL-2. In fact, this is the case.

The experiments were conducted in the pressure vessel under a He pressure of 6.2 MPa and 15°C. Known amounts of each NGL were added to the heavy oil and the mixture stirred to ensure complete mixing before the titration with n-heptane. For the high aromatics case, the plot of mL NGL per g oil vs. mL heptane per g oil gave a slope of 5.35 mL heptane per mL NGL. This slope is much higher than the 2.72 obtained using toluene as solvent, and indicates that the high aromatic NGL is an even better solvent than toluene. The results were completely different for the low aromatics NGL. At all concentrations tried with this solvent, asphaltenes were present even before addition of the heptane. This indicates an unsatisfactory diluent as expected from the high paraffin content. Ridley et al. (11), in studies with somewhat higher boiling condensates, found that heavy oil was most compatible with condensates with a higher aromatic content.

Conclusions

High aromatic NGL's would be useful as diluents for transportation of heavy oils, whereas those with a low aromatic content would probably not be suitable because of poor solvation properties.

4. CORRELATION OF ASPHALTENE PRECIPITATION PARAMETERS WITH ASPHALT STABILITY

Results and Discussion

A. Heavy Oil Experiments:

In order to complement data obtainable from Plancher's asphalt stability test (12) by employing our asphaltene precipitation techniques, initial work was directed towards understanding what is happening during all stages of the titration. Initially the same heavy oil as was used in the other phases of this work was employed.

Results are shown in Figure 7 for a solution of 4.63 mL toluene per g oil, titrated at 2 mL pentane per min. The absorbance readings were collected at 750, 800, 850 and 900 nm and joined by straight lines, giving rise to the zig-zag effect. Readings were taken at more than one wavelength in order to potentially provide additional information on asphaltene contents and particle sizes. A possible explanation for the results in Figure 7 is as follows. Asphaltenes begin to form at 12 min. when the absorbance increases dramatically. The absorbance continues to increase due to an increase in number of particles and levels off a short time after the titration with pentane has stopped. This would appear to indicate constant particle size concentration of particles has been reached as indicated by Gregory (18). When stirring of the solution is stopped at 35 min, there is an abrupt increase in absorbance which coincides with the rapid settling of the bulk of the asphaltenes as observed through the titration vessel. The upper portion of the solution remains opaque, presumably containing dispersed fine particles. A decrease in absorbance would have been expected due to the decrease in number of particles upon settling.

Alternating between stirred and unstirred solutions as shown in Figure 7 indicates that the data are reasonably repeatable. Also the relatively constant absorbance values of the stirred and unstirred solutions respectively indicates that the number and size of the particles must not be changing within each region.

A sample of the fines dispersion from one of these experiments also gave a higher absorbance when not stirred as shown in Figure 8. This indicates that particle shape might have an influence.

To see if the physical geometry of the system has a bearing on the results, the experiment was repeated using the set-up shown in Figure 1 with the solution pumped through the flow-through cell in the UV/vis spectrophotometer. Results are shown in Figure 9. The same effects are noted as when using the fiber optics probe, except after the initial increase in absorbance when stirring is stopped, there is a gradual decrease which may be due to transmitted light passing through the solution closer to the top in the flow-through cell. If time had permitted it may have been useful to investigate the settling properties of the different asphalts using this system. This experiment did however, indicate that basically similar results could be obtained with either system (fiber optics and flow-through cell).

All of these results have probably raised more questions than provided answers. However, they have been presented in the hope that they could lead to further interesting work. For the present, it was decided to use the data on the onset of asphaltene flocculation as an indicator of asphalt stability. In other words, we would test the hypothesis that for a given solvent concentration the more stable the asphalt, the more titrant would be required to reach the onset. It was also decided to investigate the use of the absorbance of the asphaltene dispersion remaining after the precipitation of the bulk as another indicator of asphalt stability.

B. Asphalt Experiments:

The asphalts were thermally treated before using in order to ensure consistency in results (19). They were heated on a hot plate for 2 h under helium to prevent oxidation. Experiments were completed within 24 h of this heat treatment.

Asphalt stability test data for three asphalts were obtained from Plancher (19). In order to ensure that the asphalts had not changed the asphalt stability test was duplicated in our laboratory. Measurements of the level

of the flocculated asphaltene dispersion in the graduated cylinder with time were made visually according to Plancher, and using the fiber optics probe placed at the mid-point of the cylinder. The probe was placed into the graduated cylinder at the mid-point mark so that the dispersion could be monitored at the same time as visual readings were obtained. The settling results for two asphalts are shown in Figure 10, and all data for three asphalts in terms of time required to settle to the mid-point of the cylinder compared to Plancher's data in Table 8. The present data compare favorably to those of Plancher. The slow settling asphalt, A-3, had a stable dispersion remaining above the initial front of asphaltenes, whereas the fast settling asphalt, A-1, was clear above the front. For A-1 the absorbance as measured by the probe remained constant for 6 min and then dropped dramatically when the level passed the bottom of the probe. It is concluded that the probe can detect the passage of the heavy asphaltene zone if the layer above is clear. For A-3 a high absorbance was measured, which remained constant for the 30 min over which it was monitored. This corresponds to the slow settling behavior of this solution.

A number of asphaltene titrations were carried out on three of the asphalt samples using n-pentane as titrant, and toluene and cyclohexane as solvents. Typical curves for each asphalt with toluene as solvent are shown in Figures 11 to 13. The main features for each case are indicated in Table 9. It can be seen that for the same solvent concentration, the more stable the asphalt dispersion, the more pentane is necessary to initiate asphaltene precipitation. This implies that the longer the asphaltenes can remain solubilized, the more compatible are the components which comprise the asphalt. This is also consistent with the solvent effect. Cyclohexane being a poorer solvent than toluene requires less pentane for precipitation to occur. Even with this solvent, the asphalts follow the same stability order.

Despite the uncertainties about explaining the absorbances of small particle dispersions, the absorbance of the dispersion remaining after the stirring is stopped and the bulk of the asphaltenes have settled also seems to correlate with the stability of the asphalt dispersion. In other words, the more stable the asphalt, the higher the absorbance of the fines dispersion. This trend seems to hold whether or not the absorbance values are corrected for

maltenes absorbance. The latter value was obtained by raising the probe up to near the top of the solution, which had more or less clarified upon completion of the experiment, and recording the reading. The turbidity of these dispersions had been noted qualitatively by Plancher (19) but could not be quantitated.

The asphalts were also analyzed by thin layer chromatography with flame ionization detection. The results shown in Table 10 indicate a correlation between aromatic content and asphalt stability. The more stable the asphalt (or less tendency for asphaltene precipitation), the higher the aromatic content. As already mentioned, aromatics are known as good solubilizers for asphaltenes.

This asphalt stability study required more work than anticipated, partly by the attempts to sort out the effects of particle size and absorbance of dispersions. In any event there was not sufficient time left to carry out the asphalt modifier study.

Conclusions

The results obtained by monitoring the absorbance of heavy oil and asphalt solutions in toluene and cyclohexane as pentane is added, leave many unanswered questions, such as why the absorbance of asphalt dispersions increase when stirring is stopped. However, there does appear to be a correlation between asphalt stability, as measured by Plancher's test, and both the asphaltene precipitation tendency and the absorbance of the asphalt dispersion remaining at the completion of the experiment. Furthermore, the total aromatic content of the asphalt appears to be correlated with asphalt stability.

Recommendations

The experiments to study the effect of modifiers on asphalt stability should be carried out. Some of the other unexplainable findings such as the increase in absorbance of the asphalt dispersion when stirring is stopped, should be investigated further.

ACKNOWLEDGEMENTS

The authors would like to thank Laura Phibbs of Chemex Labs (Alberta) Ltd. for some of the experimental work, and Henry Plancher from Western Research Institute, Laramie, Wyoming, for supplying the asphalt samples.

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TABLE 1A

Asphaltene Flocculation Data for Primary Production and Fireflood Heavy Oils

Sample	Intercept (mL pentane/g oil)	Std. Dev.	Slope (mL pentane/mL toluene)	Std. Dev.
Primary Production				
P-1/87	2.18	0.26	2.06	0.01
Fireflood				
F-1/85	1.46	0.33	1.94	0.02
F-1/87	1.22	0.20	2.26	0.01
F-2/87	2.10	0.05	2.07	0.01

TABLE 1B

Analytical Data for Primary Production and Fireflood Heavy Oils

	Primary Production P-1/87	Fireflood F-1/85	Fireflood F-1/87	Fireflood F-2/87
Density (g/mL @ 25°C)	0.9735	0.9228	0.9415	0.9724
Viscosity (cPs @ 25°C)	3340	55.7	280	2880
Distillation (vol %)				
Naphtha (115-204°C)	3.0	25.2	14.2	4.9
Mid-Dist (204-345°C)	19.8	23.3	24.1	19.5
Gas Oil (345-442°C)	15.0	13.4	13.0	14.7
Resid (>442°C)	62.2	38.1	48.7	60.9

TABLE 2

Asphaltene Flocculation Data for Vacuum Bottoms Feedstocks

Sample	Intercept (mL pentane/g resid.)	Std. Dev.	Slope (mL pentane/mL toluene)	Std. Dev.
30-IPPL-84	2.47	0.17	2.05	0.01
35-IPPL-86	1.72	0.23	2.01	0.02
29-B24-83	2.43	0.38	2.03	0.02
26-EB-81 + 975	0.47	0.10	2.07	0.01
25-ARA-81 FNG	3.26	0.40	1.85	0.03

TABLE 3

Slopes of Asphaltene Flocculation Curves at Different Pressures and Temperatures Using Helium and Carbon Dioxide

Gas	Pressure (MPa)	Temperature (°C)	Slope (mL heptane/mL toluene)
He	Atmospheric	15	2.72
	0.69	15	2.83
	2.07	15	2.64
	4.83	15	2.84
CO_2	0.69	15	1.93
	2.76	15	0.35
	2.76	51	1.03
	2.76	105	1.42

TABLE 4

CO_2 Pressure Required to Initiate Asphaltene Precipitation in Heavy Oil Solution in the Absence of Heptane

mL Toluene/g Heavy Oil	Pressure (MPa)
3.97	4.69
5.38	4.41
9.47	3.86

TABLE 5

Slopes of Asphaltene Flocculation Curves at Different Pressures and Temperatures Using Propane

Temperature (°C)	Pressure (MPa)	Slope (mL heptane/mL toluene)
15	Atmospheric	2.72
	0.35	1.69
	0.52	1.17
50	0.52	1.60

TABLE 6
Component Analysis of High Aromatic Natural Gas Liquid

Component	Boiling Point (°C)	Mole Fraction	Mass Fraction	Volume Fraction
Nitrogen	-196	0.0000	0.0000	0.0000
Carbon Dioxide	-79	0.0000	0.0000	0.0000
Hydrogen Sulphide	-60	0.0000	0.0000	0.0000
Methane	-162	0.0000	0.0000	0.0000
Ethane	-89	0.0000	0.0000	0.0000
Propane	-42	0.0008	0.0003	0.0005
Iso-Butane	-12	0.0013	0.0006	0.0009
N-Butane	-1	0.0000	0.0000	0.0000
Iso-Pentane	28	0.0025	0.0015	0.0021
N-Pentane	36	0.0061	0.0036	0.0049
Hexanes	69	0.0119	0.0084	0.0109
Heptanes	98	0.0217	0.0193	0.0224
Octanes	126	0.0333	0.0332	0.0375
Nonanes	151	0.0274	0.0304	0.0336
Decanes	174	0.0340	0.0414	0.0450
Undecanes	196	0.1020	0.1340	0.1436
Dodecanes	216	0.0478	0.0675	0.0715
Tridecanes	236	0.0178	0.0267	0.0280
Tetradecanes	253	0.0157	0.0250	0.0260
Pentadecanes	271	0.0137	0.0228	0.0236
Hexadecanes	287	0.0161	0.0281	0.0289
Heptadecanes	302	0.0057	0.0106	0.0109
Octadecanes	317	0.0048	0.0095	0.0097
Nonadecanes	331	0.0028	0.0058	0.0059
Eicosanes	334	0.0014	0.0031	0.0031
Heneicosanes	357	0.0008	0.0019	0.0020
Docosanes	369	0.0012	0.0030	0.0030
Tricosanes	380	0.0005	0.0011	0.0011
Tetracosanes	391	0.0006	0.0015	0.0015
Pentacosanes	402	0.0003	0.0009	0.0009
Hexacosanes	412	0.0000	0.0000	0.0000
Heptacosanes	422	0.0000	0.0000	0.0000
Octacosanes	432	0.0000	0.0000	0.0000
Nonacosanes	441	0.0000	0.0000	0.0000
Triacosanes+	449	0.0000	0.0000	0.0000
Benzene	80	0.0860	0.0592	0.0534
Toluene	111	0.3036	0.2465	0.2256
Xylene	139	0.1415	0.1324	0.1205
1,2,4-Trimethylbenzene	179	0.0070	0.0077	0.0070
Cyclopentane	49	0.0003	0.0002	0.0002
Methyl Cyclopentane	72	0.0094	0.0070	0.0073
Cyclohexane	81	0.0339	0.0251	0.0256
Methyl Cyclohexane	101	0.0481	0.0417	0.0429
Totals		1.0000	1.0000	1.0000

TABLE 7
Component Analysis of Low Aromatic Natural Gas Liquid

Component	Boiling Point (°C)	Mole Fraction	Mass Fraction	Volume Fraction
Nitrogen	-196	0.0000	0.0000	0.0000
Carbon Dioxide	-79	0.0000	0.0000	0.0000
Hydrogen Sulphide	-60	0.0000	0.0000	0.0000
Methane	-162	0.0000	0.0000	0.0000
Ethane	-89	0.0061	0.0011	0.0025
Propane	-42	0.0280	0.0072	0.0115
Iso-Butane	-12	0.0106	0.0036	0.0052
N-Butane	-1	0.0431	0.0145	0.0203
Iso-Pentane	28	0.0242	0.0101	0.0132
N-Pentane	36	0.0356	0.0149	0.0193
Hexanes	69	0.0583	0.0291	0.0356
Heptanes	98	0.0715	0.0499	0.0539
Octanes	126	0.0748	0.0581	0.0613
Nonanes	151	0.0469	0.0408	0.0421
Decanes	174	0.0605	0.0576	0.0584
Undecanes	196	0.0510	0.0525	0.0524
Dodecanes	216	0.0417	0.0460	0.0455
Tridecanes	236	0.0411	0.0483	0.0472
Tetradecanes	253	0.0387	0.0481	0.0466
Pentadecanes	271	0.0346	0.0451	0.0435
Hexadecanes	287	0.0270	0.0369	0.0353
Heptadecanes	302	0.0286	0.0417	0.0398
Octadecanes	317	0.0230	0.0354	0.0335
Nonadecanes	331	0.0165	0.0268	0.0252
Eicosanes	334	0.0168	0.0294	0.0277
Heneicosanes	357	0.0154	0.0284	0.0267
Docosanes	369	0.0135	0.0253	0.0237
Tricosanes	380	0.0135	0.0261	0.0244
Tetracosanes	391	0.0108	0.0216	0.0200
Pentacosanes	402	0.0106	0.0220	0.0204
Hexacosanes	412	0.0091	0.0192	0.0179
Heptacosanes	422	0.0087	0.0191	0.0176
Octacosanes	432	0.0081	0.0182	0.0168
Nonacosanes	441	0.0079	0.0183	0.0169
Triacosanes+	449	0.0123	0.0293	0.0270
Benzene	80	0.0022	0.0012	0.0010
Toluene	111	0.0075	0.0048	0.0041
Xylene	139	0.0291	0.0213	0.0181
1,2,4-Trimethylbenzene	179	0.0118	0.0101	0.0086
Cyclopentane	49	0.0006	0.0003	0.0003
Methyl Cyclopentane	72	0.0215	0.0125	0.0123
Cyclohexane	81	0.0108	0.0063	0.0060
Methyl Cyclohexane	101	0.0280	0.0189	0.0182
Totals		1.0000	1.0000	1.0000

TABLE 8
Asphalt Stability Data by Test of Plancher

	Half-height time (min)		
	A-1	A-2	A-3
Plancher	9.5	13.5	50.5
Present Work	7.0		44.0

TABLE 9
Asphaltene Flocculation Data for Asphalts

	A-1	A-2	A-3
Solvent: Toluene			
Conc. (mL/g asphalt)	7.38	7.26	7.52
Floc. Thresh. (mL pent/g)	14.5	16.8	18.5
Fines Abs. (with maltenes corr.)	1.2	2.0	2.0
Conc. (mL/g asphalt)	4.50		4.68
Floc. Thresh (mL pent/g)	9.30		11.2
Fines Abs. (no maltene corr.)	2.0		3.1
Solvent: Cyclohexane			
Conc. (mL/g asphalt)	7.47		7.71
Floc. Thresh (mL pent/g)	5.70		9.20
Fines Abs. (with maltenes corr.)	1.4		2.1

TABLE 10
Aromatic Content of Asphalts by TLC/FID

	Aromatics (wt%)	Std. Dev. (wt%)
A-1	39	1
A-2	44	1
A-3	46	1

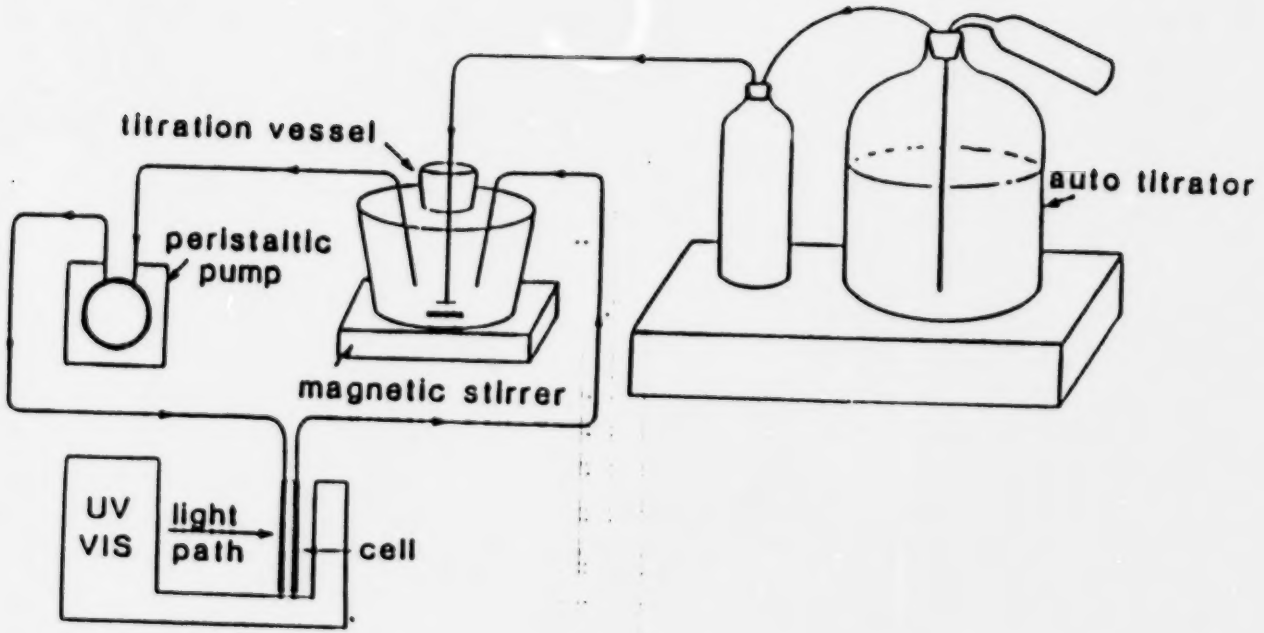


Figure 1: Schematic diagram of the asphaltene flocculation measurement system.

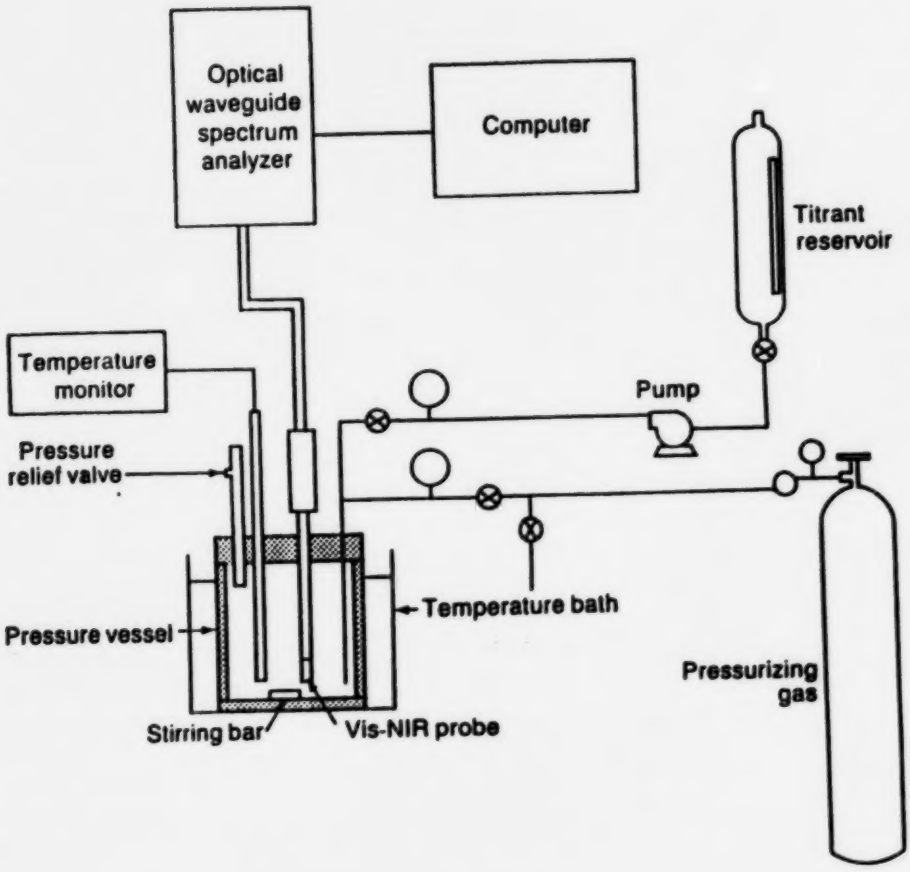


Figure 2: Schematic of apparatus for asphaltene flocculation experiments at elevated temperatures and pressures.

Figure 3: Plots of amount of n-pentane required to initiate asphaltene precipitation vs concentration of toluene in heavy oils.

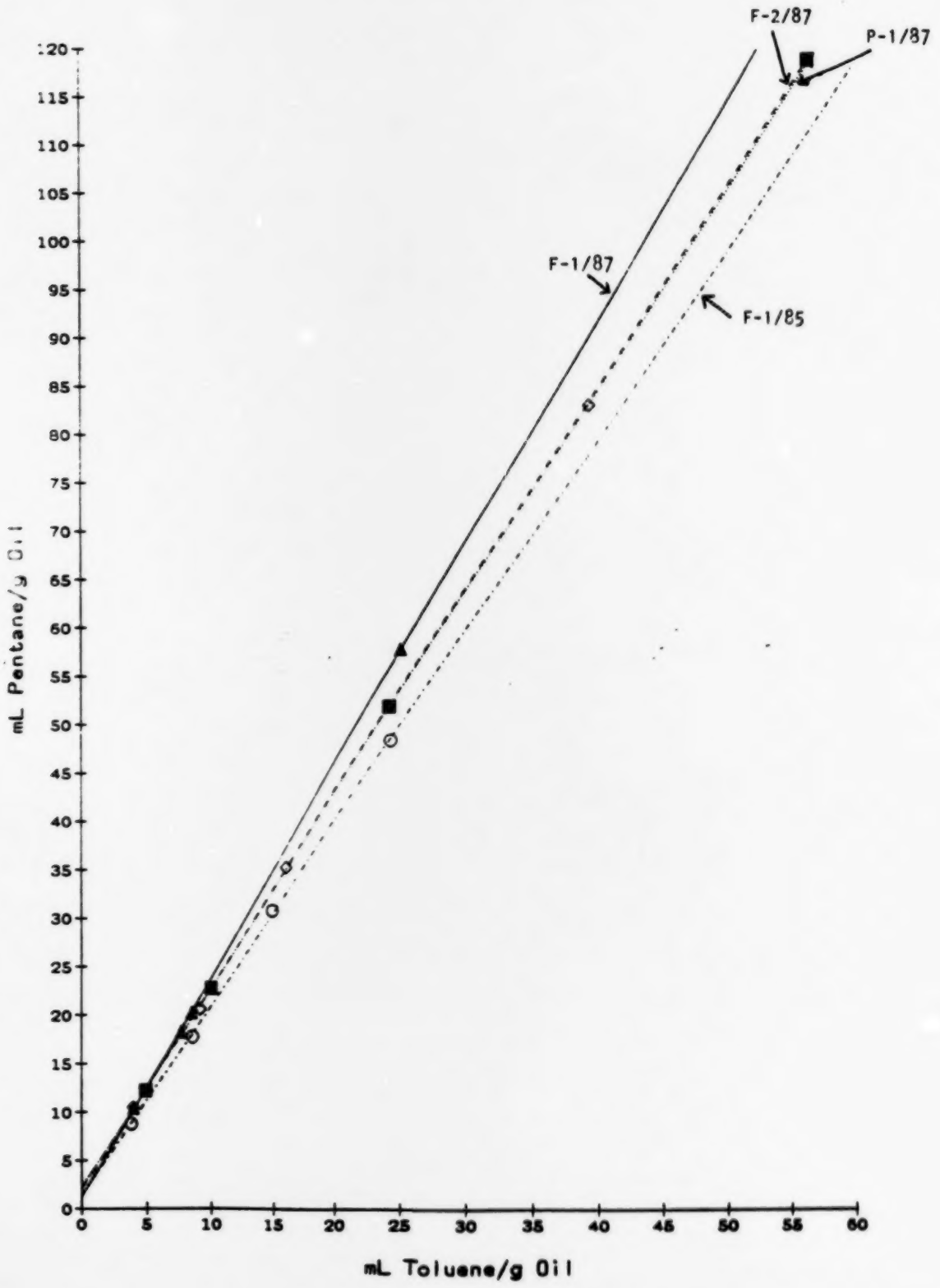


Figure 4: Plots of amount of n-heptane required to initiate asphaltene precipitation vs concentration of toluene in heavy oil at different CO_2 pressures.

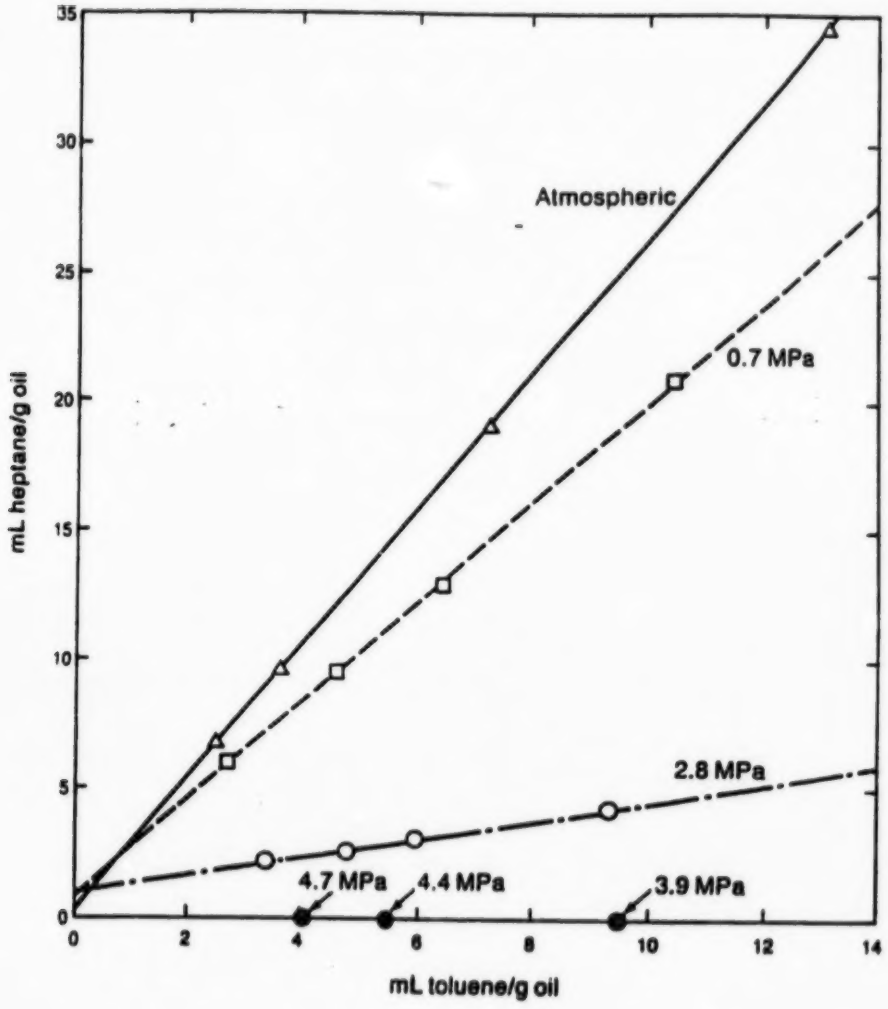
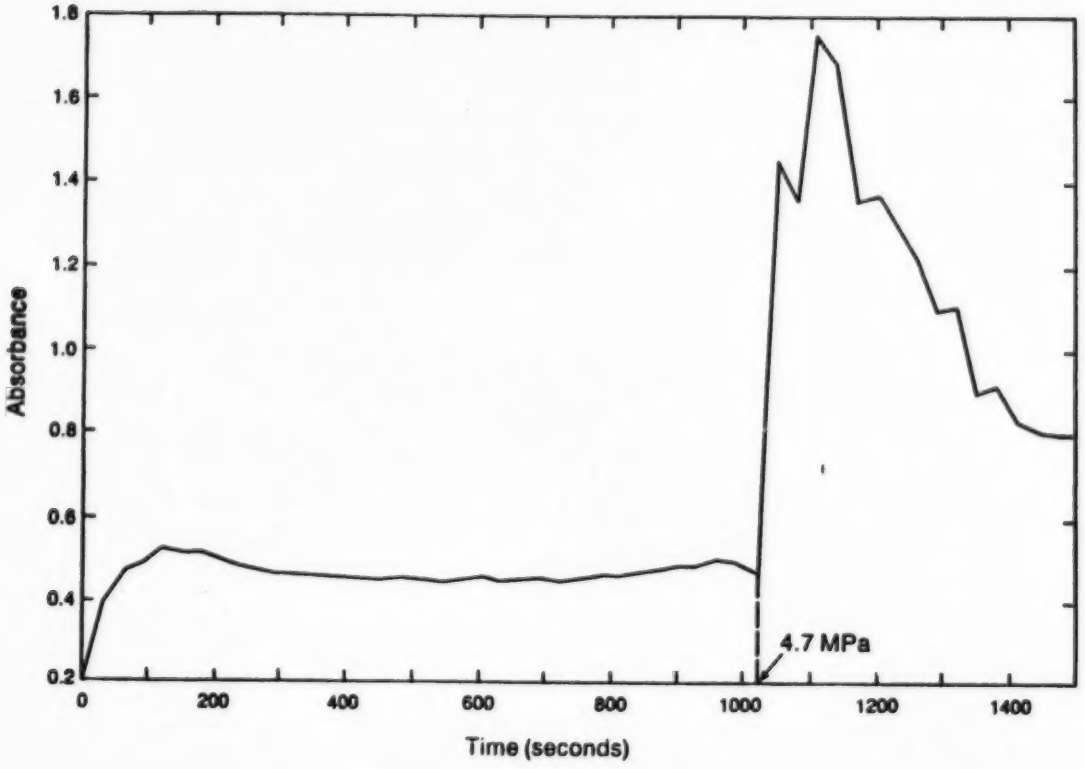


Figure 5: Plot of absorbance of heavy oil in toluene solution vs time at a 0.28 MPa/min increase in CO_2 pressure indicating asphaltene onset at 4.7 MPa.



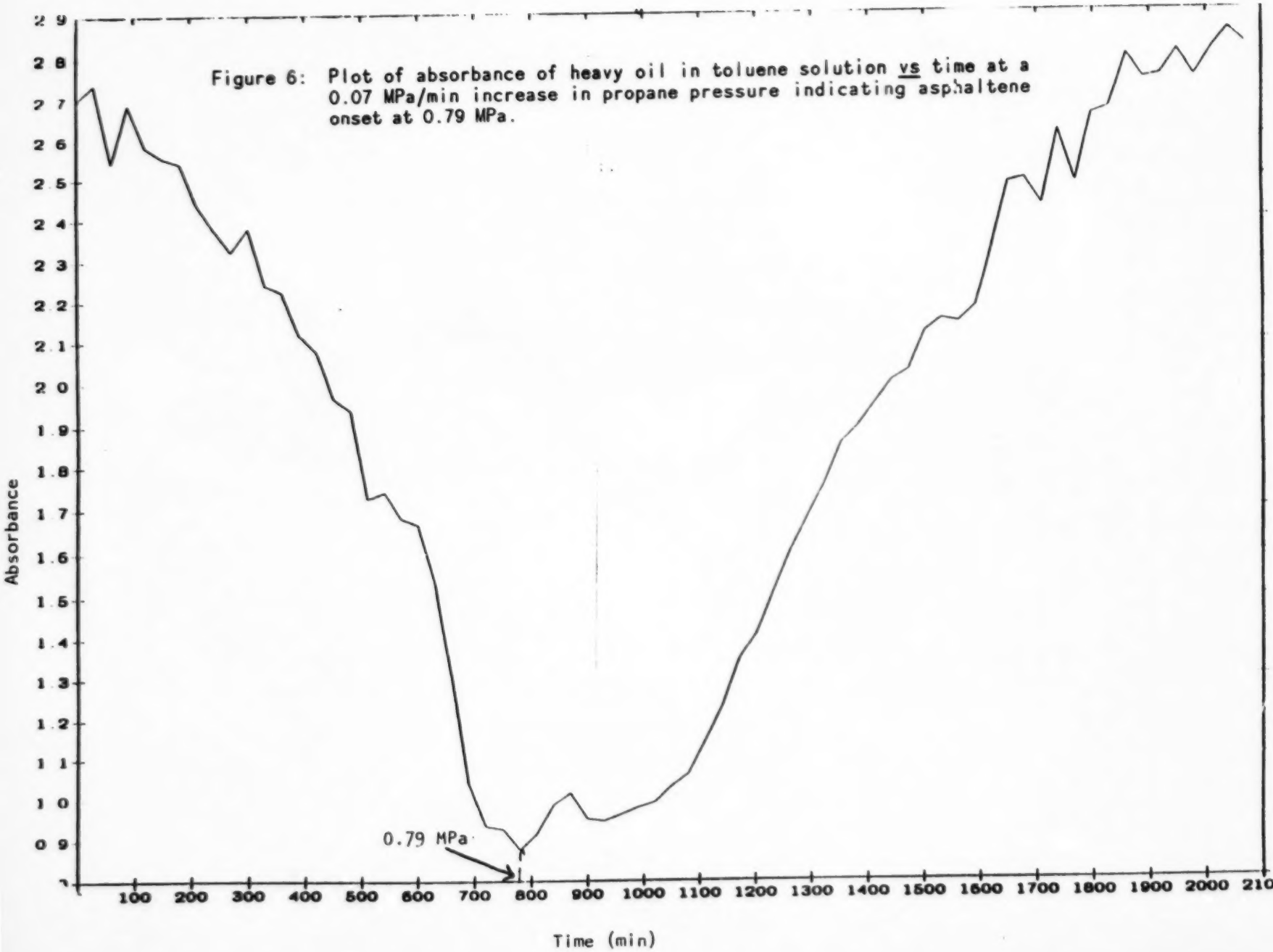


Figure 6: Plot of absorbance of heavy oil in toluene solution vs time at a 0.07 MPa/min increase in propane pressure indicating asphaltene onset at 0.79 MPa.

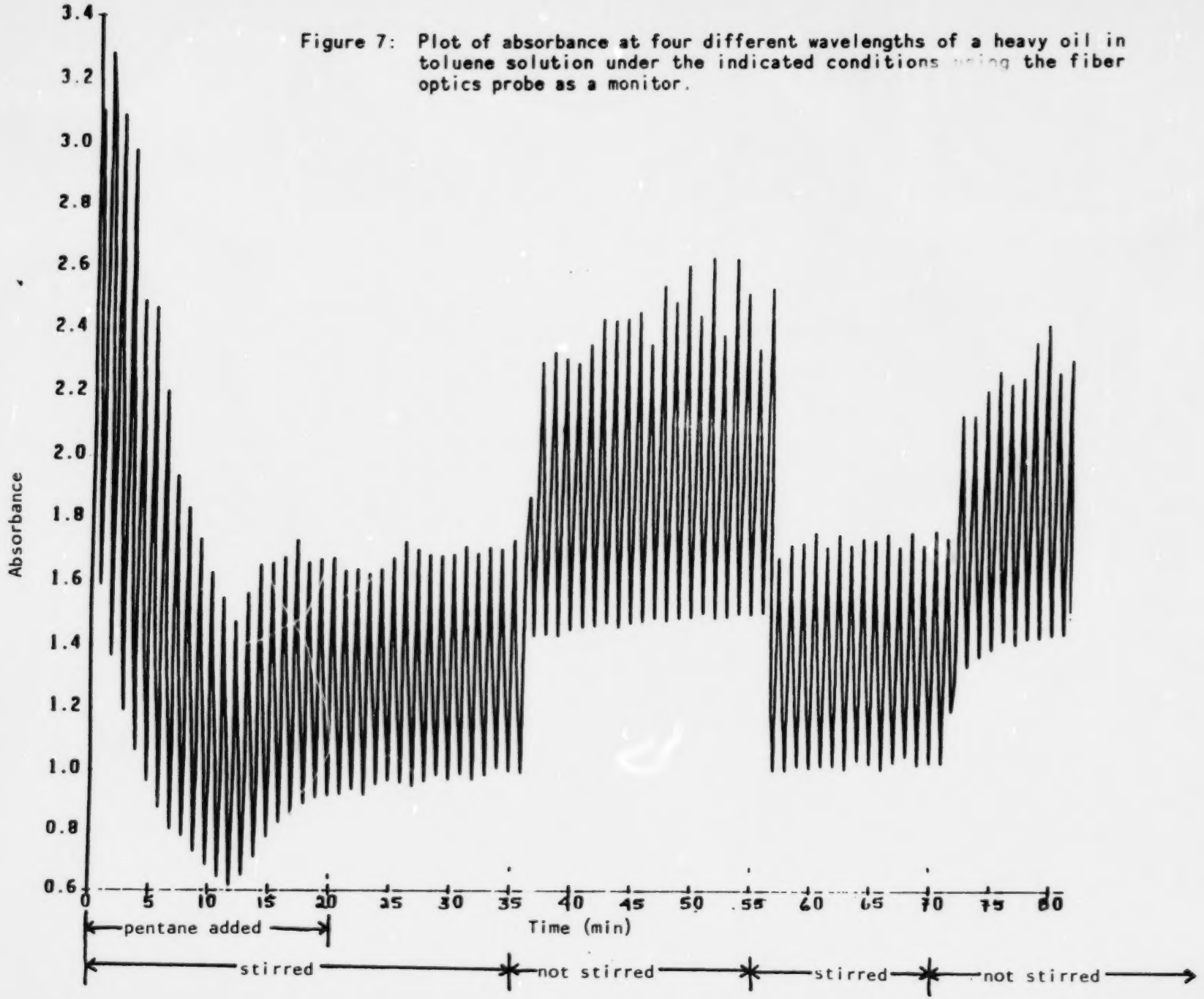


Figure 7: Plot of absorbance at four different wavelengths of a heavy oil in toluene solution under the indicated conditions using the fiber optics probe as a monitor.

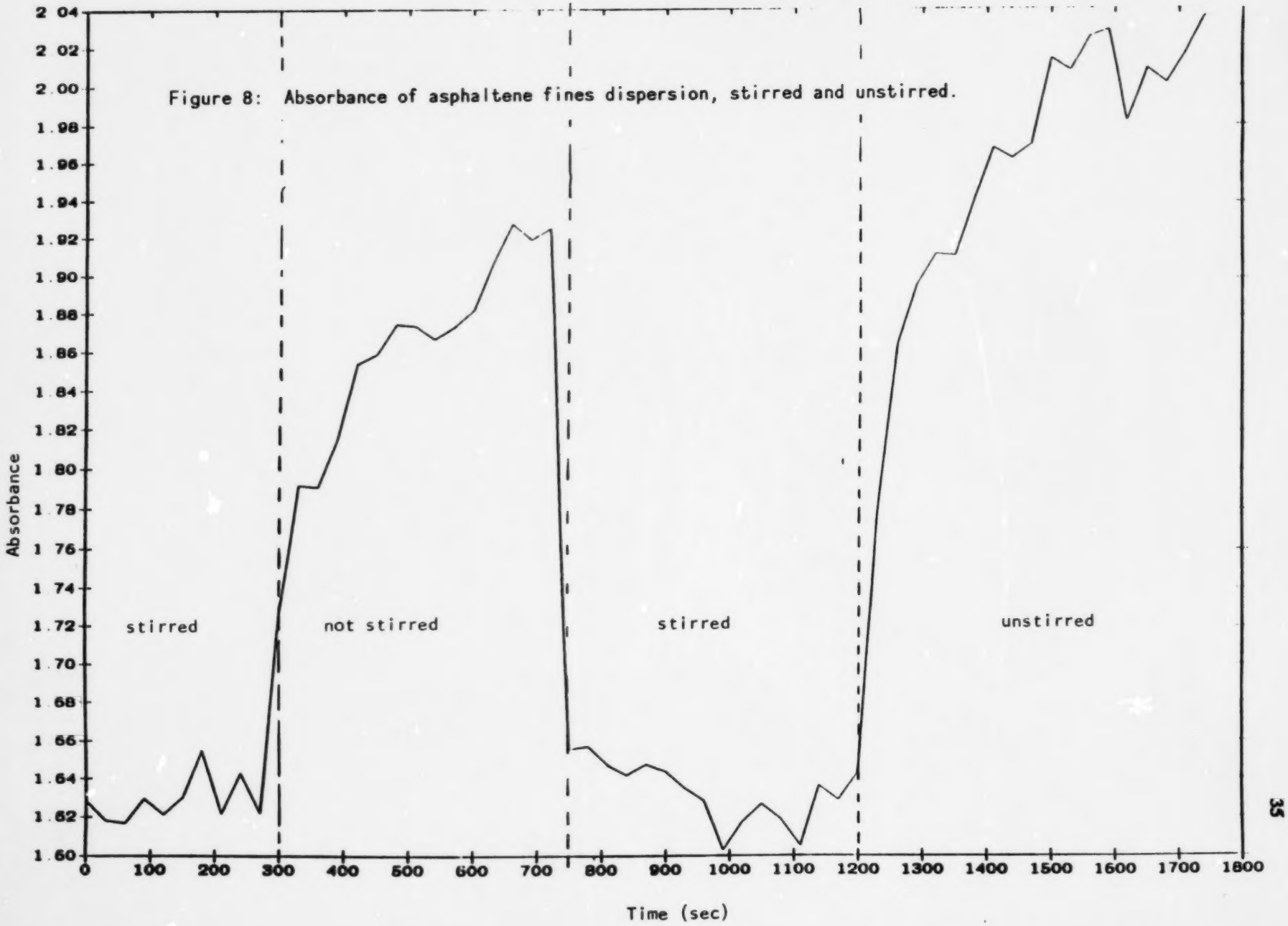


Figure 8: Absorbance of asphaltene fines dispersion, stirred and unstirred.

Figure 9: Plot of absorbance at 800 nm of a heavy oil in toluene solution under the indicated conditions using the visible spectrophotometer and flow-through cell.

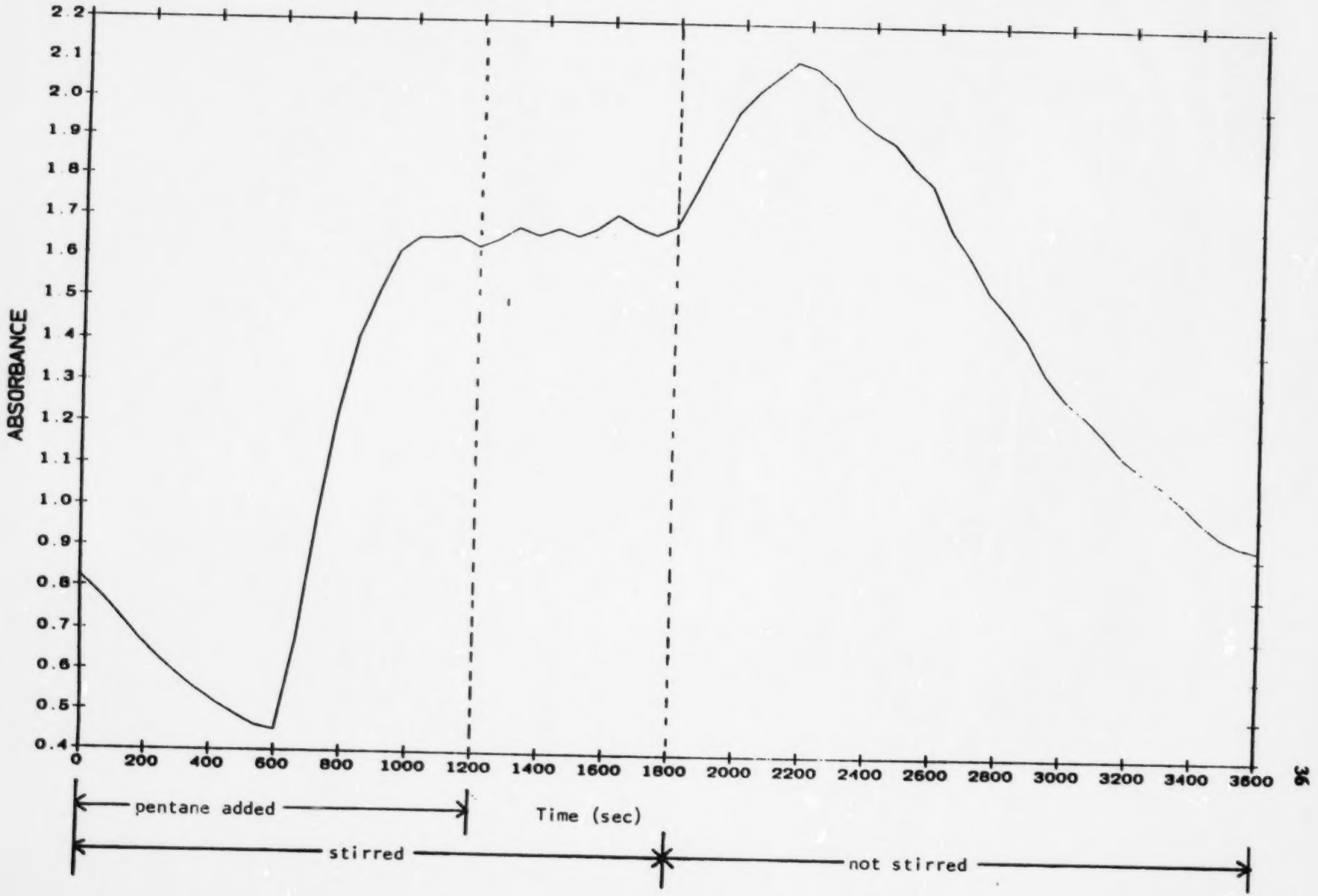
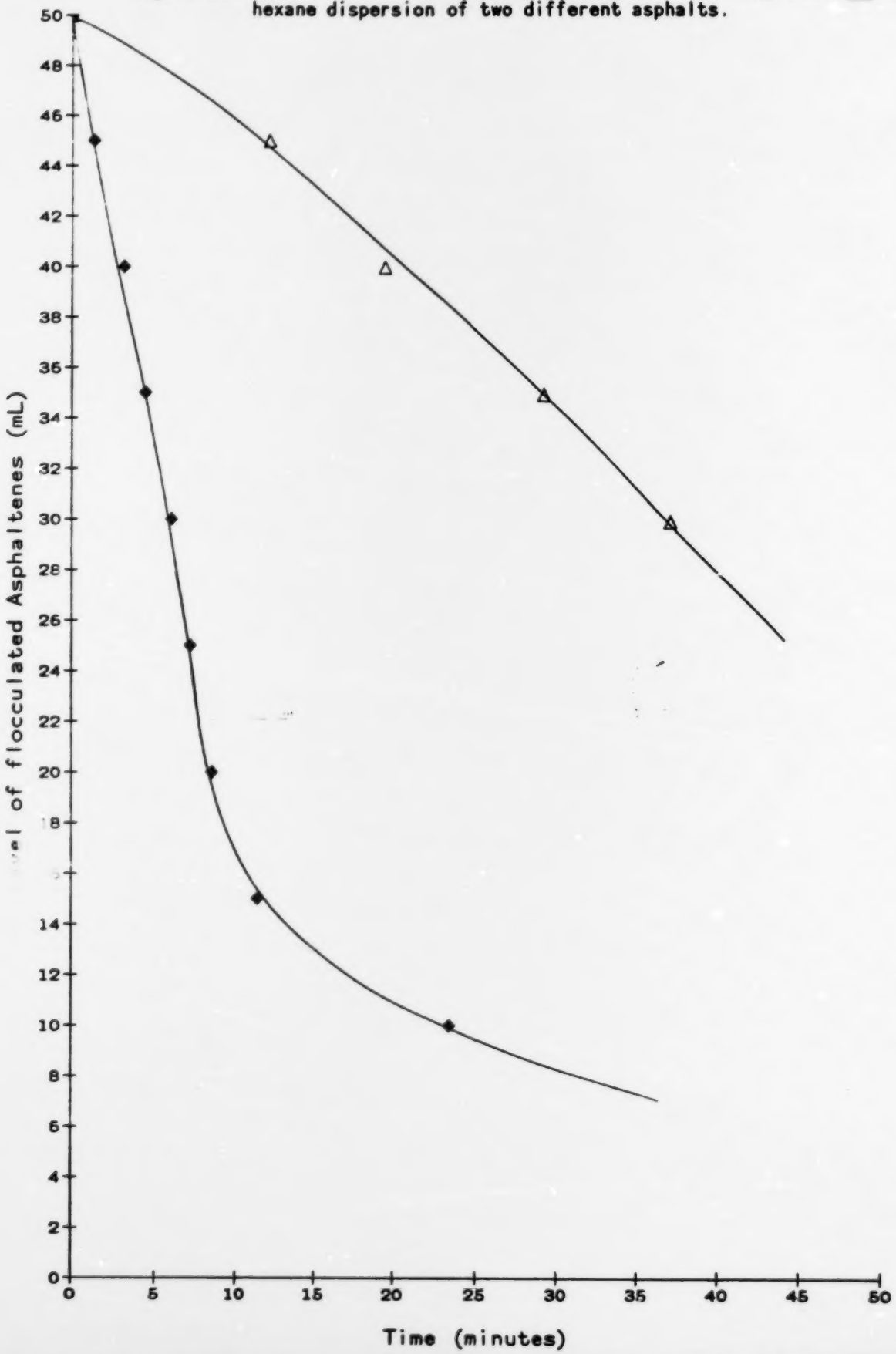


Figure 10: Level of flocculated asphaltenes in settling tube vs time for hexane dispersion of two different asphalts.



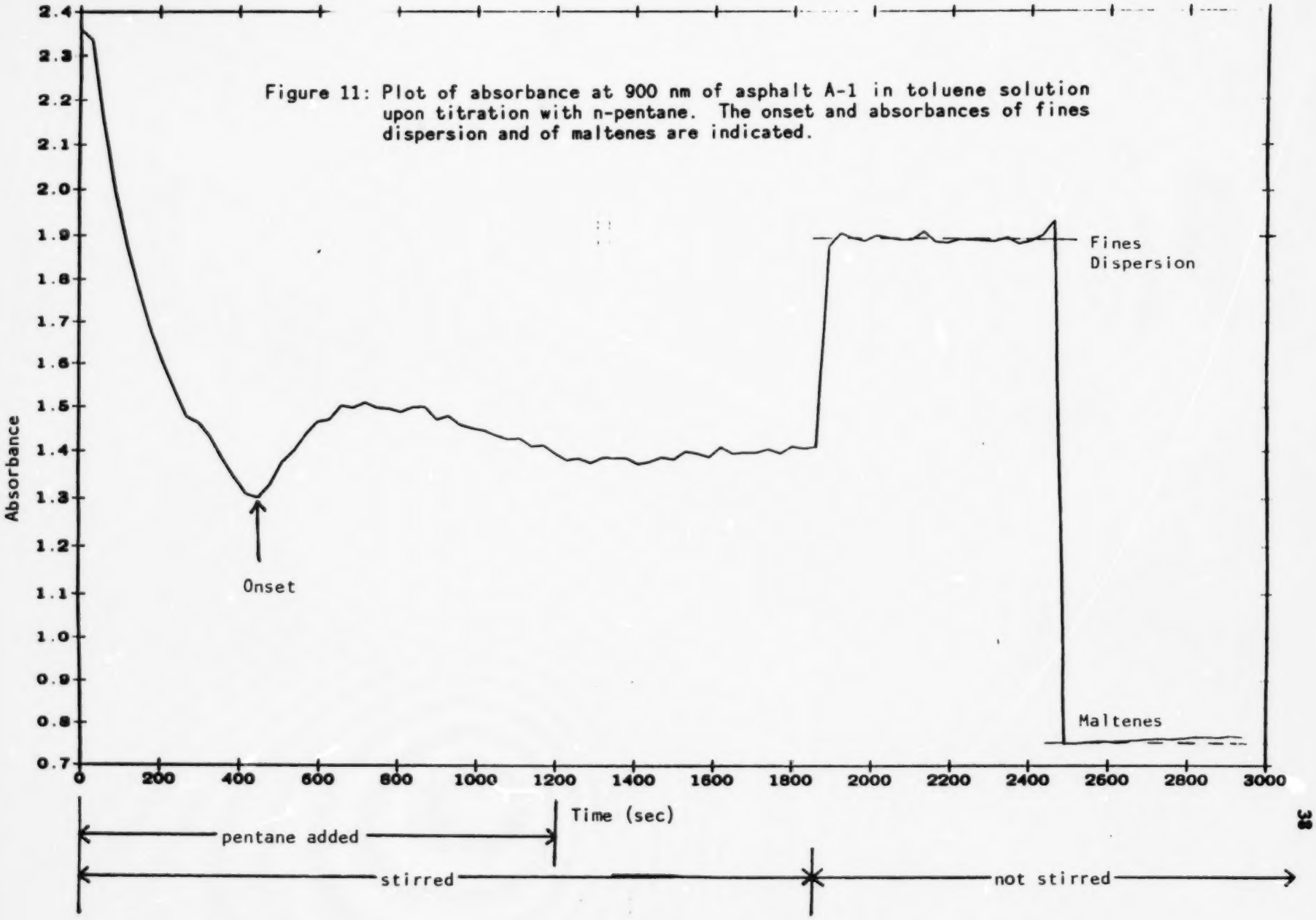


Figure 11: Plot of absorbance at 900 nm of asphalt A-1 in toluene solution upon titration with n-pentane. The onset and absorbances of fines dispersion and of maltenes are indicated.

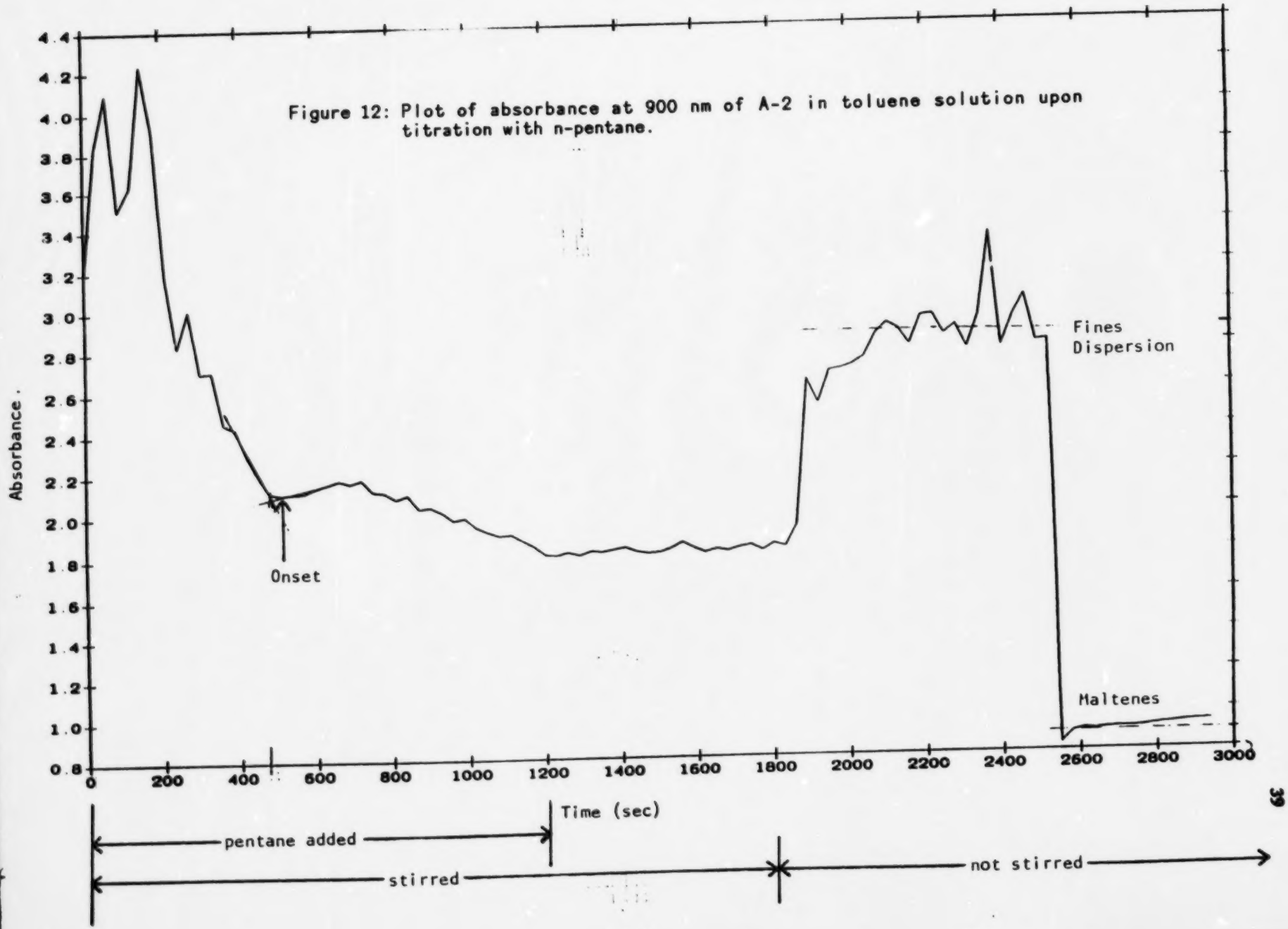


Figure 12: Plot of absorbance at 900 nm of A-2 in toluene solution upon titration with n-pentane.

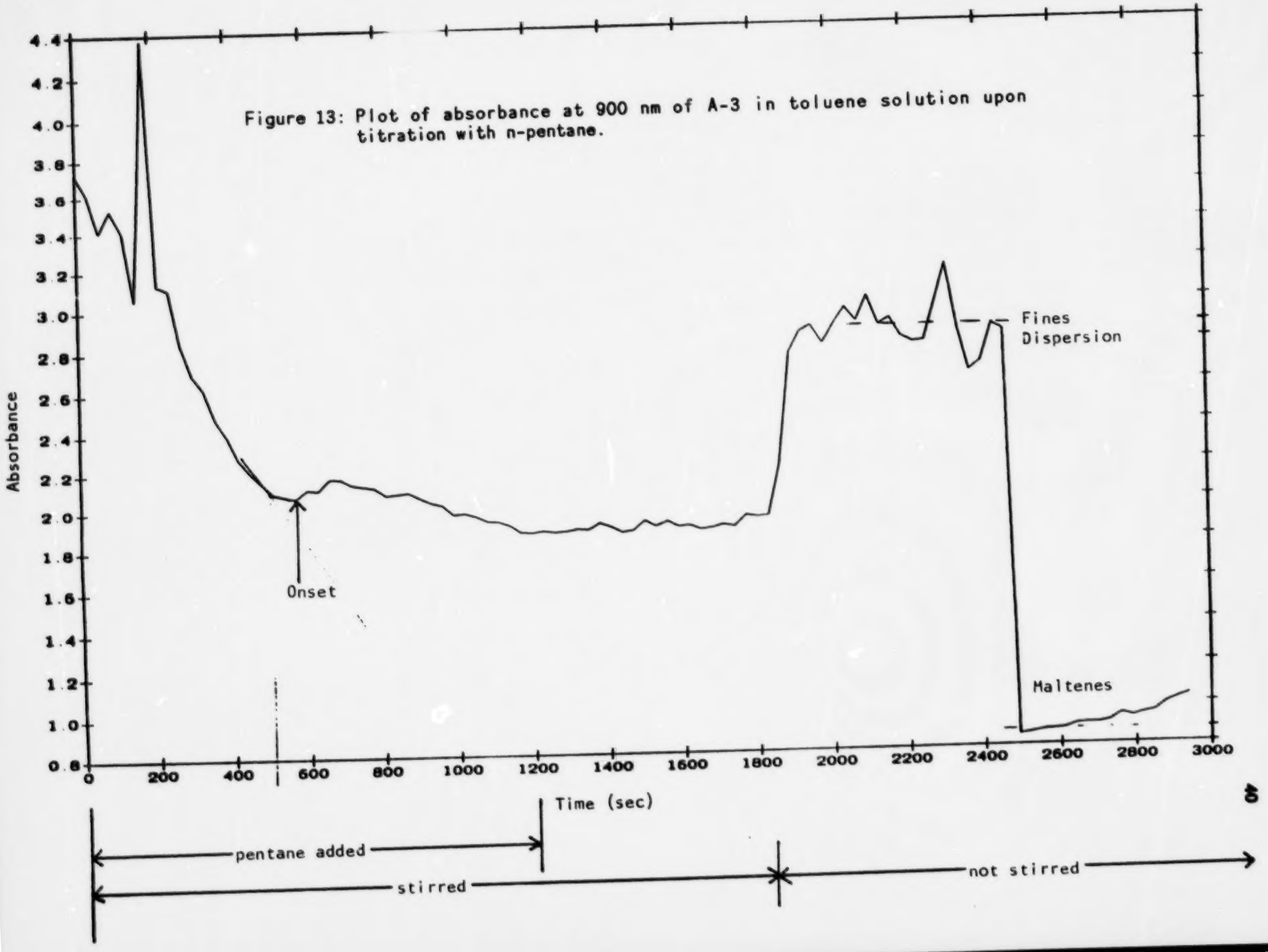


Figure 13: Plot of absorbance at 900 nm of A-3 in toluene solution upon titration with n-pentane.